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FLAMMABILITY OF HETEROGENEOUSLY COMBUSTING METALS

Prepared By: Peter D. Jones, Ph.D., P.E.

Academic Rank: Associate Professor

Institution and Department: Auburn University
Mechanical Engineering Department

NASA/MSFC:

Laboratory: Materials and Processes
Division: Metallic Materials and Processes
Branch: Metallurgical Research and Development

MSFC Colleague: Biliyar N. Bhat, Ph.D.

INTRODUCTION

Most engineering materials, including some metals, most notably aluminum, burn in homogeneous combustion. 'Homogeneous' refers to both the fuel and the oxidizer being in the same phase, which is usually gaseous. The fuel and oxidizer are well mixed in the combustion reaction zone, and heat is released according to some relation like

$$q_c = \Delta H_c C \left(\frac{P}{P_0} \right)^a \exp \left(\frac{-E_c}{RT} \right) \quad (1)$$

where the pressure exponent a is usually close to unity. As long as there is enough heat released, combustion is sustained. It is useful to conceive of a threshold pressure beyond which there is sufficient heat to keep the temperature high enough to sustain combustion, and beneath which the heat is so low that temperature drains away and the combustion is extinguished.

Some materials burn in heterogeneous combustion, in which the fuel and oxidizer are in different phases. These include iron and nickel based alloys, which burn in the liquid phase with gaseous oxygen. Heterogeneous combustion takes place on the surface of the material (fuel). Products of combustion may appear as a solid slag (oxide) which progressively covers the fuel. Propagation of the combustion melts and exposes fresh fuel. Heterogeneous combustion heat release also follows the general form of Eq.(1), except that the pressure exponent a tends to be much less than 1. Therefore, the increase in heat release with increasing pressure is not as dramatic as it is in homogeneous combustion. Although the concept of a threshold pressure still holds in heterogeneous combustion, the threshold is more difficult to identify experimentally, and pressure itself becomes less important relative to the heat transfer paths extant in any specific application. However, the constants C , a , and E_c may still be identified by suitable data reduction from heterogeneous combustion experiments, and may be applied in a heat transfer model to judge the flammability of a material in any particular actual-use situation.

In order to support the above assertions, two investigations are undertaken: 1) PCT data are examined in detail to discover the pressure dependence of heterogeneous combustion experiment results; and 2) heterogeneous combustion in a PCT situation is described by a heat transfer model, which is solved first in simplified form for a simple actual-use situation, and then extended to apply to PCT data reduction (combustion constant identification).

PROPAGATION RATE DATA

PCT burned length is difficult to predict with a heat transfer model because of the dripping phenomena. As the rod burns, a ball of molten metal covered by slag forms at its tip. When the slag is heavy enough, it sloughs off, pulling some of the molten metal with it. If there is enough molten metal left behind, and if it is hot enough, then

combustion will continue because there is enough heat released by the combustion reaction over the active surface to defeat radiative and other losses. If the molten remainder is too small or too cool, it will extinguish. The temperature of the remainder, even if given knowledge of the transient temperature field in the melt, is governed by the time or conditions under which separation (sloughing) occurs. The size of the remainder is governed by the complex viscous and attractive interactions of the sloughing slag and the fixed solid sample. Models have not yet been developed which can predict either phenomenon with any precision. Therefore, burned length results cannot at present be used to identify the constants of the combustion reaction rate equation.

Heat transfer models of heterogeneous combustion situations [2,3] are more readily written to simulate the approximate temperature fields and the propagation rates of the flame front or melt interface for a steadily advancing combustion, given the physical and thermophysical properties of the metal and the form and constants of the combustion reaction rate. The propagation rate is an experimentally observable quantity, and can be used to correlate simulation with experiment. (Temperature fields in the burning, slag-covered molten metal are difficult to observe. Infrared measurements of the molten region in some PCTs have been acquired [4], though these measurements average radiant intensity over the entire molten region, and thus represent a bulk mean of T^4 . This could also be a useful quantity for correlation, though capability for this measurement is not yet present at MSFC.)

The propagation rate of a PCT test may be determined from a suitable video record of the test by measuring the length of the unconsumed rod as a function of time (using a 0.01 s resolution time display, a jog VCR, and a scale factor for length measured on the video screen). This has been done for a variety of materials and is reported in ref.[5]. It is found that the propagation rate as a function of test time is fairly constant, and that there is relatively little scatter in the propagation rate from one observably identical sample to another. Therefore, propagation rate is a conveniently observable quantity which may be conveniently used to correlate between experimental and simulated results in order to identify the constants of the combustion reaction rate equation.

Propagation rate as presently reported on MSFC PCT data sheets shows a large uncertainty. This is because propagation rate is presently derived from the measured burn length divided by the difference between very nominal test start and stop times. To make propagation rate data useful, a more automated version of the above procedure must be instituted. For instance, clear (well filtered) video records could be made of all tests (currently, only one test cell has an adequate video setup), and visible pointers at a measured distance apart could be placed in the plane of the sample. Change in length over change in time could then be easily computed.

The propagation rate data in ref.[5] are presented as functions of PCT chamber pressure, and exponential functions are fit. It is found that in heterogeneous combustion of the samples considered (low alloy steels, stainless steels, nickel alloys, cobalt alloys),

the pressure exponent of this fit is between 0.18 and 0.49. Thus pressure dependence is relatively flat (as compared to homogeneous combustors), and threshold pressure will be difficult to identify experimentally.

PCT THERMAL MODEL

A heat transfer (thermal) model of the PCT test is presented in ref.[3]. This model does not include slag build-up on the fuel/oxidizer interface, and is thus subject to temperature instabilities. The instabilities were temporarily solved with an ignition temperature (imposed constant temperature for the combustion reaction). This model is completed with the addition of combustion-limiting slag build-up terms. In the solid zone, energy conservation is written

$$\begin{aligned} \rho_s c_s A_s \left[\frac{\partial T}{\partial t} + (s-1) \frac{V}{l_s} \frac{\partial T}{\partial s} \right] \\ = \frac{k_s A_s}{l_s^2} \frac{\partial^2 T}{\partial s^2} - P_s h_s (T - T_w) - P_s \epsilon_s \sigma_b (T^4 - T_w^4) \end{aligned} \quad (2)$$

The left side of Eq.(2) represents advective transport (the phase interface between solid and liquid is fixed and serves as the origin). The coordinate system thus moves and stretches (as the solid is consumed), and the von Mises transformation must be applied. The right side first term is conduction, the second term is convection from the surface, and the third is radiation. The boundary conditions are adiabatic at the far end, and melting temperature at the phase interface. Variables are $T(s)$ and V . The convection coefficient arises from a cold vertical surface heated by a hot vertical surface below it [6]. In the liquid zone, energy conservation is written

$$\begin{aligned} \rho_l c_l A_l \left[\frac{\partial T}{\partial t} + (1-x) \frac{V}{l_x} \frac{\partial T}{\partial x} \right] \\ = \frac{k_l}{l_x^2} \left(A_l \frac{\partial^2 T}{\partial x^2} + \frac{dA_l}{dx} \frac{\partial T}{\partial x} \right) - P_l h_x (T - T_w) \\ - P_l \sigma_b (T^4 - T_w^4) + P_l q_c \end{aligned} \quad (3)$$

where combustion heat release has been added to the right side. The variables are $T(x)$ and V . Boundary conditions are adiabatic at the far end, and melting temperature at the phase interface. The propagation rate V is defined by the interface condition

$$V = \frac{1}{\rho_s h_{sl}} \left[\frac{k_s}{l_s} \frac{\partial T}{\partial s} \Big|_{s=0} + \frac{k_l}{l_x} \frac{\partial T}{\partial x} \Big|_{x=0} \right] \quad (4)$$

The combustion heat release is moderated by build-up of slag (combustion product), which reduces the concentration of oxygen on the molten metal surface. Oxygen penetrates the slag by diffusion, and the slag layer acts as a diffusive resistance to oxygen concentration, thus

$$q_c = \Delta H_c \left\{ \left[C \left(\frac{p}{p_0} \right)^2 \exp \left(\frac{-E_c}{RT} \right) \right]^{-1} + \frac{\delta}{\rho_s D} \right\}^{-1} \quad (5)$$

The slag thickness is related to the combustion reaction rate and is also defined on the moving, stretching coordinate system

$$\begin{aligned} \frac{\partial \delta}{\partial t} + (1-x) \frac{V}{l_x} \frac{\partial \delta}{\partial x} \\ = \frac{1}{\rho_s} \left\{ \left[C \left(\frac{p}{p_0} \right)^2 \exp \left(\frac{-E_c}{RT} \right) \right]^{-1} + \frac{\delta}{\rho_s D} \right\}^{-1} \end{aligned} \quad (6)$$

In the solid rod, cross sectional area and perimeter are constant. In the liquid ball, these are functions of x

$$\begin{aligned} A_x &= \pi (1-x) (r^2 + x l_x^2) \\ P_x &= 2 (\pi A_x)^{1/2} \end{aligned} \quad (7)$$

where the length of the liquid zone is defined from continuity by

$$\frac{dl_x}{dt} = \frac{2 \rho_s A_s V}{\pi \rho_x (l_x^2 + r^2)} \quad (8)$$

The model of Eqs.(2-8) is solved in discrete form using a full matrix solver for $T(s)$, $T(x)$, and V . (Iterative solution between T and V tends to diverge). Nonlinear terms, including T/V cross terms are linearized by Taylor series about set points, and the solution is iterated to converge the linearization points. After convergence, the simulation is marched in time.

The model was initially simplified to steady state, with constant liquid cross section and perimeter, to provide a solution development case. Such a case represents a simple actual-use situation of steady combustion of a flat sheet with a line of combustion going all the way across it. Simulations were successful, showing a positive propagation rate, a solid temperature profile rising to the interface, a liquid temperature profile rising from the interface under the influence of combustion and then falling as the building slag layer inhibited further combustion, and a slag layer thickness building to a downstream asymptote (resolidification downstream was not simulated). If the combustion rate constants were reduced, the propagation rate slowed or went negative (negative rate is a degenerate case in the model, and physically represents extinguishment). The simple simulation was found to be very sensitive to D , which is itself a function of temperature [7]

$$D = D_0 \exp \left(\frac{-\Delta H_p}{RT} \right) \quad (9)$$

Equation (9) represents an extrapolation to combustion temperatures (1800 to 3000 K for iron) from data peaking at 1500 K. This is a shortcoming of the model, since oxygen diffusion through slag has a great impact on the simulation, and yet very little is known about diffusion through high temperature oxides lying on liquid metals. It must be kept in mind that accurate simulation requires good physical understanding, and that the mechanisms of heterogeneous combustion are at the edge of our knowledge. High temperature diffusion through combustion products is one of the detailed issues which lie on this edge. Further study of high temperature diffusion through oxide is warranted.

The model of Eqs.(2-8) was then prepared for transient PCT simulation to roughly identify the combustion rate constants. This application proved to be less stable than the steady, one-dimensional simplification. Stable solutions could only be obtained through careful selection of starting linearization points and ultra-slow under-relaxation (successive under-relaxation coefficient of 0.02). Since the model was implemented on WATFOR Fortran on a 33 MHz PC, this meant a run of at least overnight for the first time step, and several days to complete a full drop growth and separation cycle. Unfortunately, it was discovered after these runs that the time and stretching terms in Eq.(6) had been neglected (the slag thickness was solved as a function of x only, using a Runge-Kutta projection at each linearization point). Correcting this oversight will require more time than remains to the author at MSFC, at the time that this report is written.

RECOMMENDATIONS

In the near term, it is recommended that the MSFC PCT operational procedure be modified to allow presentation of data as in ref.[5]. Knowledge of the variation of combustion propagation rate with pressure will allow an extra dimension of understanding in the material selection of heterogeneous combustors. Thermal models of a few generic actual-use situations should be constructed, such as burning edge, burning wedge, and burning plate (two-dimensional) should be built. These generic models would help in quantifying the correlation between hanging rod (burning pin) PCT experiments and actual-use situations.

In the middle term, the use of PCT experiments and simulations to identify combustion rate equation constants should be put on a firmer computational and intuitive basis. Computational aspects include more appropriate software, hardware, and optimal parameter identification algorithms. Intuitive aspects include justifiable model simplifications and a basic understanding of result sensitivities. With these in hand, consideration might be given to replacement of threshold pressure material ranking with combustion rate equation comparisons.

In the longer term, the fundamentals of heterogeneous combustion should be better understood. In particular, high temperature diffusion through oxide layers, a key to heterogeneous combustion behavior, requires investigation.

